

Thermochemical measurement of the ligand field splitting energies for hexaaquo complexes of Mn(II), Ni(II) and Zn(II) ions in the Tutton's salts.

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Tutton's salt – ligand field splitting energies – heat of solution;
Heat of solution – of Tutton's salts.

RINGKASAN

Beberapa hidrat garam Tutton Mn(II), Ni(II) dan Zn(II) yang bertenaga tinggi dan juga berhablur biasa telah disediakan dan haba larutannya disukat. Nilai beza tenaga pada garam kontang telah diberikan sebagai kJ/mol heksahidrat dan dianggarkan sebagai 10Dq bagi kompleks-kompleks tersebut. Nilai-nilai ini telah dibandingkan dengan tenaga pemecahan medan ligand bagi kompleks-kompleks itu dalam garam sulfat. Sisihan tenaga ini telah ditapsirkan sebagai akibat keujudan ion-ion ammonium dalam kekisi yang mungkin telah merendahkan ketumpatan elektron dalam molekul-molekul air koordinatan.

SUMMARY

Various high-energy modification and crystalline hydrates of Tutton's salts containing Mn(II), Ni(II) and Zn(II) have been prepared and their heats of solution measured. The energy difference of the anhydrous salts given in kJ/mole of hexahydrate have been assigned as 10Dqs for the complexes. The values obtained have been compared with the ligand field splitting energies of the complexes in the sulphate salts. The discrepancies were explained in terms of the presence of ammonium ions in the lattice which may have reduced the electron density on the coordinated water molecules.

INTRODUCTION

A number of investigations of the thermochemical measurement of the ligand field splitting energy have been reported (Jamieson *et al.*, 1965, Badri and Jamieson, 1970, 1977, 1979). For the *aquo* complexes, the technique involves the measurement of the heats of solution of various crystalline hydrates and their corresponding high-energy modifications which were prepared by dehydration *in vacuo*. In each case, the difference in their heats of solution at the monohydrate composition was expressed in kilocalories per mole of the heptahydrate. The values obtained agree quite well with 10Dq's found by the spectroscopic method. This agreement suggests the validity of the technique.

The present paper shall report on the recent measurements for the hexaaquo complexes in

the double salts of general formula $(\text{NH}_4)_2\text{SO}_4 \cdot \text{MSO}_4 \cdot 6\text{H}_2\text{O}$ where M = Mn(II), Ni(II) and Zn(II). The results obtained for the cases where M = Fe(II), Co(II) and Cu(II) have been reported elsewhere (Badri and Hussein, 1979) but a brief mention shall be made for the purpose of clarity and comparison.

According to their crystal structures, the water molecules in the salts are coordinated to the central metal ions (Huckel, 1950) to form distorted octahedral complexes. For M = Fe(II) and Cu(II), (Bowers and Owen, 1955, Montgomery and Lingafelter, 1966, Webb *et al.*, 1965) the average M-OH₂ bond lengths are shorter compared to the average M-OH₂ bond lengths found in the sulphate salts FeSO₄ · 7H₂O and CuSO₄ · 5H₂O (Baur, 1964, Beevers and Lipson, 1934). Thus one would expect that

$10Dq$'s for the complexes in the double salts to be larger. Similarly, for $M = \text{Ni(II)}$ and Zn(II) , (Montgomery and Lingafelter, 1964, 1963) the average metal ligand bond lengths in the double salts are longer compared to those in the sulphate salts (Beevers and Lipson, 1934, 1932). Thus one would expect the $10Dq$'s to be smaller. Unfortunately, for $M = \text{Mn(II)}$ and Co(II) , no detailed structures are available to us for comparison.

The spectrum for the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ in the double salt ferrous ammonium sulphate has been reported (Cotton and Meyer, 1964). The value for $10Dq$ was given as $9.6 \times 10^3 \text{cm}^{-1}$ which agrees very well with that found by the calorimetric method (Badri and Hussein, 1979). The thermochemical technique was also applied to the double salts of Cu(II) and Co(II) . Even though the values obtained were of the right order of magnitude, the relationship of their heat of solution data with the percent water content of the salts was found to differ significantly. It was found that in each case of the crystalline hydrates of cupric ammonium sulphate and cobaltous ammonium sulphate, the heats of solution fall on a single straight line in going from the hexahydrate to the respective anhydrous salts. These results, together with the present ones, have led us to reconsider the interpretation of the heat of solution data for the ferrous ammonium sulphate and the heats of transition between the high-energy and low-energy modifications of the hydrates of the double salts. The differences in the $10Dq$'s obtained for the complexes in the double salts and the sulphate salts shall be discussed in terms of the presence of the ammonium ions in the outer coordination sphere.

EXPERIMENTAL

The starting materials used were the hexahydrates of the double salts. $(\text{NH}_4)_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ was supplied by B.D.H., $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was supplied by Hayashi Pure Chemical Industries, and $(\text{NH}_4)_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 6\text{H}_2\text{O}$ was supplied by Wako Pure Chemical Industries. The water content of each salt was checked by thermogravimetric analysis. The results agree well with the theoretical values except for the manganese(II) salt where the experimental value is found to be 26.00% compared to the theoretical value of 27.60%. The experimental values were used for the purpose of subsequent calculations.

For the preparation of the lower crystalline hydrates, the hexahydrates were heated in an oven at various temperatures for various time intervals. The high-energy modification hydrates were prepared by dehydrating the hexahydrate *in vacuo* at a pressure of less than 1×10^{-4} torr for various time intervals. The percentage of water in each product was calculated by the loss in weight. The heat of solution was measured immediately.

The calorimeter used for the measurement of the heats of solution was made up of a plastic bucket of diameter 22 cm. A small plastic bottle was cut to house a 300 ml silvered Dewar flask. The bottle was glued to the centre of the bucket and the space in between was filled with decanoic acid (m.p. 31°C). It was then covered with a wooden cover with two small holes made to accommodate thermocouple reference junctions. The Dewar flask was fitted with a cover with holes to accommodate the hot junctions of thermocouples, a stirrer, a 5-ohm heater made of chromel wire and a glass funnel for sample delivery. About 200 ml of distilled water was used as solvent. The whole assembly was immersed in a water bath thermostatted at 31°C . The thermocouples were connected to a micro-voltmeter with an output to a recorder.

RESULTS

The heats of solution obtained are tabulated in Tables 1, 2 and 3 for double salts of Mn(II) , Ni(II) and Zn(II) respectively and are plotted as a function of percent water in the salts in Figs. 1, 2 and 3. In each case, the heats of solution for the crystalline hydrates fall on a single straight line BA in going from the hexahydrate to the anhydrous salt. Similarly, the heats of solution for the high energy modification hydrates fall on a higher heat of solution line BC.

Mn(II)

Using the method of least squares, the equations for the lines BA and BC in Fig. 1 have been found to be

$$y_{\text{BA}} = 139 - 8.95x$$

$$y_{\text{BC}} = 245 - 13.0x$$

From the line BA, the heat of solution for the hexahydrate of manganese(II) ammonium sulphate has been estimated to be -149 J/g , at D. The line DE has been drawn parallel to the line BC with the equation

$$y_{\text{DE}} = 251 - 13.0x$$

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TABLE 1

Heats of solution for the hydrates of manganese ammonium sulphate

Percent water in salt	Heat of solution J/g	Method of Preparation
0	149	heat at 122°C
0.09	135	110°C
2.18	115	88°C
3.77	102	88°C
5.37	88.8	83°C
7.60	67.3	83°C
12.00	31.8	83°C
14.67	22.1	83°C
18.53	— 28.1	70°C
26.00	— 94.6	hexahydrate vacuum
0.0	242	"
3.38	203	"
7.47	152	"
10.66	110	"
13.77	63.1	"
17.17	20.5	"
17.96	11.5	"

The line DE represents the highest possible heat of solution line for high-energy modification hydrates of manganese ammonium sulphate with the hexahydrate as the starting material. Thus the highest possible heat of transition for the anhydrous salt is 112 J/g which is equivalent to $3.66 \times 10^3 \text{cm}^{-1}$ per mole of hexahydrate.

Ni(II)

The equations for the lines BA and BC in Fig. 2 are

$$y_{BA} = 264 - 13.4x$$

$$y_{BC} = 394 - 17.9x$$

The heat of solution for the crystalline anhydrous salt at A is 264 J/g and that for the high-energy modification anhydrous salt at C is 394 J/g. Thus the heat of transition at the composition of the anhydrous salt is 130 J/g which is equivalent to $4.30 \times 10^3 \text{cm}^{-1}$ per mole of hexahydrate.

Zn(II)

The equations for the lines BA and BC in Fig. 3 are

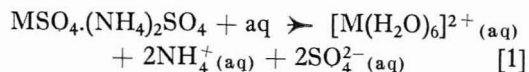
$$y_{BA} = 167 - 9.83x$$

$$y_{BC} = 263 - 13.3x$$

The heat of solution for the crystalline anhydrous salt at A is 167 J/g and that for its high-energy modification at C is 263 J/g. Thus the heat of transition from C to A is 96 J/g anhydrous salt which is equivalent to $3.23 \times 10^3 \text{cm}^{-1}$ per mole of hexahydrate.

DISCUSSION

It is evident that incorporation of ammonium sulphate into the lattice of anhydrous metal(II) sulphate stabilizes the latter. The amount of stabilization can be calculated from the enthalpy changes for the following reactions:



ΔH_1 = heat of solution for the anhydrous double salt.

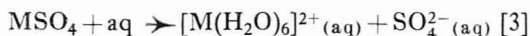


ΔH_2 = heat of solution for ammonium sulphate

TABLE 2

Heats of solution for the hydrates of nickel ammonium sulphate

Percent water in salt	Heat of solution J/g	Method of preparation
0.0	265	heat at 226°C
2.65	228	226°C
2.92	236	226°C
3.65	214	200°C
4.43	207	159°C
4.69	205	159°C
5.29	191	167°C
5.44	191	153°C
6.36	175	167°C
6.82	172	167°C
7.93	165	159°C
9.05	156	153°C
10.59	131	153°C
14.75	61.1	132°C
15.03	54.4	159°C
15.19	62.4	136°C
16.58	39.7	136°C
17.60	31.6	132°C
19.42	11.6	136°C
23.55	— 54.6	120°C
25.51	— 83.4	120°C
27.10	— 105	110°C
27.19	— 92.5	120°C
27.34	— 106	hexahydrate vacuum
3.46	329	"
4.72	301	"
13.71	155	"
17.41	87.9	"
20.17	39.9	"
20.41	42.1	"
23.08	— 22.5	"
25.24	— 69.5	"
26.67	— 91.5	"



ΔH_3 = heat of solution for the anhydrous metal sulphate.

By adding 3 to 2 and subtracting 1.



$$\Delta H = \Delta H_3 + \Delta H_2 - \Delta H_1$$

Since the heat of solution for ammonium sulphate is $9.91 \times 10^{-3} \text{ kJ/mol}$ (Mellors, 1927)

$$\Delta H = \Delta H_3 - 9.91 \times 10^{-3} - \Delta H_1$$

The various values of ΔH obtained this way are given in Table 4. All systems show stabilization except for Fe(II) which shall be discussed later.

TABLE 3

Heats of solution for the hydrates of zinc ammonium sulphate

Percent water in salt	Heat of solution J/g	Method of preparation
0.0	168	heat at 123°C
4.31	127	121°C
13.39	39.0	111°C
13.97	35.1	111°C
18.57	-17.1	97°C
19.23	-27.7	97°C
21.10	-39.4	111°C
21.44	-40.9	111°C
21.76	-42.7	97°C
22.09	-47.4	111°C
22.71	-54.3	111°C
24.44	-68.3	87°C
26.89	-97.8	hexahydrate vacuum
0.36	-264	"
0.57	257	"
1.91	238	"
5.80	188	"
7.07	167	"
7.36	165	"
9.06	138	"
12.39	103	"
16.09	52.3	"
16.18	49.5	"
17.94	28.9	"
20.67	-12.7	"
20.96	-18.2	"

same. So the ligand field stabilization energy resulting should be about the same and therefore the amount of the extra-stabilization in the double salt would be very small, if any. However even in the cases of Mn(II) and Zn(II) this stabilization is considerable. It is well known that there is no ligand field stabilization energy in these two systems. Thus it is more likely that the extra-stabilization is the result of electrostatic interactions between ions in the anhydrous double salt.

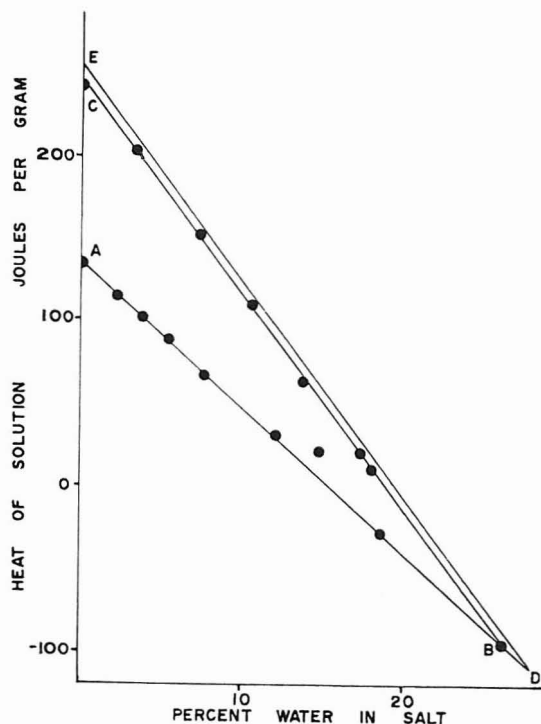


Fig. 1 Heats of solution for the hydrates of manganese ammonium sulphate.

In the anhydrous salt, it is possible that the metal(II) ions are surrounded by six oxygen atoms from the sulphate ions. Since the sulphate ions are bigger than the metal ions, the crowding may result in a considerable repulsion. Ammonium ions in the double salt would act as shields to reduce the repulsion either by virtue of their positive charges or more likely by forming an extensive hydrogen bond system throughout the crystal. Hydrogen bonding would reduce the intensity of the negative charge on the sulphate ions and therefore the mutual repulsion would also be reduced. The salt thus becomes more stable.

While a rigorous analysis is difficult to give here because of lack of information about the crystal structures, a qualitative picture could be presented. This stabilization might be due to the ligand field of the coordinated sulphate ions in the crystal of the anhydrous salt. However, in both cases of metal(II) sulphates and the double salts, the coordinated species are the

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TABLE 4

Heats of solution for some anhydrous metal(II) sulphates and double salts.

M	MSO ₄ kJ/mole	(NH ₄) ₂ SO ₄ · MSO ₄ kJ/mole	Stabilization kJ/Mole
M = (NH ₄ ⁺) ₂	9.91 × 10 ⁻³	—	—
Mn	61.35	39.36	21.99
Fe	62.31	76.74 (39.79)	-14.43 (22.51)
Co	92.76	70.74	22.44
Ni	92.42	75.74	16.68
Cu	63.41	55.87	7.54
Zn	72.39	49.02	23.37

In all cases, except for Fe(II), the crystalline hydrates have their heats of solution falling on a single straight line in going from the hexahydrate to the anhydrous salt. This is contrary to what has been found for the hydrates of metal(II) sulphates (Jamieson *et al.*, 1965) and the hydrates of Fe(II) double salt (Badri and Hussein, 1979). In each of these cases there is a change in the slope of the heat of solution line for the crystalline hydrates in going from the starting material to the anhydrous salt. For Fe(II) double salt, an increase of the slope occurs at the dihydrate composition whereas in the case of metal(II) sulphate the increase occurs at the monohydrate composition. In the latter, the increase in the slope was attributed to the fact that the water molecule in the monohydrate is anionic. The heat of solution line is a measure of the strength of the chemical bonds between the water molecules and the ions in the salt, hence the change in the slope. Thus we can conclude that all the water molecules in the double salts are primarily held by coordination. Even though their crystal structures indicate the possibility of hydrogen bonding, the extent is probably limited by other factors to be discussed later.

In Table 4, the stabilization energy due to the formation of ferrous ammonium sulphate from iron(II) sulphate and ammonium sulphate is a negative quantity. However, if the heat of solution line for the crystalline materials were extrapolated to the anhydrous composition, the value of heat of solution for the anhydrous salt is obtained as 39.79 kJ/mole (bracketed). With this, the stabilization energy would then be 22.51 kJ/mole. This value conforms to the

other values obtained for the other double salts and therefore perhaps it should be used for the calculation of the ligand field splitting energy for hexaaquoiron(II) in the double salt. With this, the recalculated $10Dq$ is $10.4 \times 10^3 \text{cm}^{-1}$ which is the same as those found for the complex

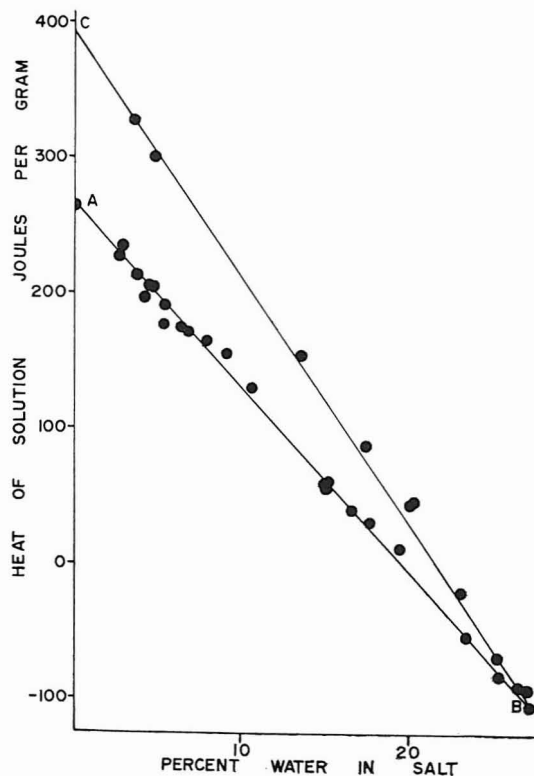


Fig. 2 Heats of solution for the hydrates of Nickel ammonium sulphate.

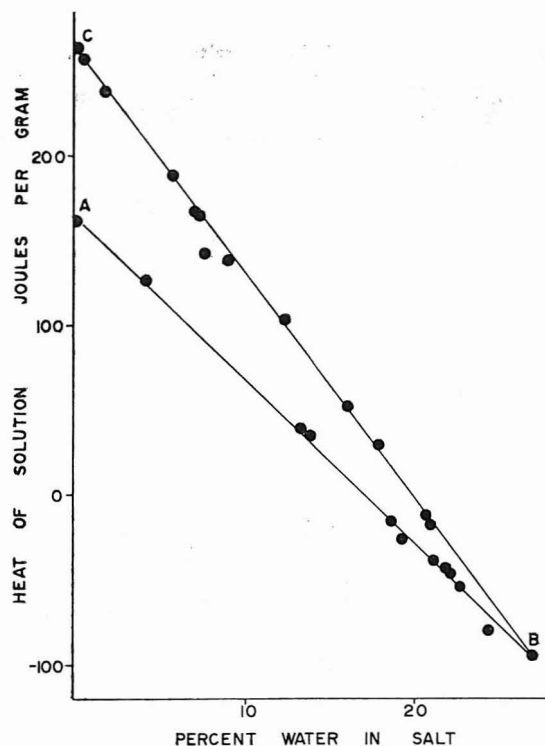


Fig. 3 Heats of solution for the hydrates of Zinc ammonium sulphate.

in aqueous solution (Orgel, 1965) and in the sulphate salt (Jamieson *et al.*, 1965).

The values of $10Dq$ obtained for Mn(II), Ni(II) and Zn(II) in the double salt are considerably smaller than those obtained for the hexaaquocomplexes in the sulphate salts and aqueous solution even though they are of the same order of magnitude. For ease of comparison they are tabulated in Table 5. The values for Fe(II), Cu(II) and Co(II) are quite consistent with those found in sulphate salts. In fact for Fe(II) and Cu(II) they should be higher because of shorter M-OH₂ bond lengths. In the case of Co(II) we can thus assume that the bond lengths are shorter and similarly in the present three cases the bond lengths are longer compared to those present in the corresponding sulphate salts.

The results for Cu(II) and Fe(II) point to a more fundamental difference in the electrical environments around the metal ions in the sulphate salt and the double salt. While the symmetry of the ligand field can influence the

TABLE 5

Ligand field splitting energy for hexaaquocations by calorimetric method

Metal	Sulphate salt $\times 10^3 \text{cm}^{-1}$	Double salt $\times 10^3 \text{cm}^{-1}$
Mn	7.7	3.66
Fe	10.4	10.4
Co	9.1	9.43
Ni	8.4	4.30
Cu	11.6	9.37
Zn	8.3	3.23

splitting of the d-orbitals, perhaps in the two situations discussed, the effect is minimal. This is because in the hydrated form, the metal ions in both situations are enveloped fully by the octahedrally coordinated water molecules. The potential felt by the metal ions due to the sulphate ions in the outer coordination sphere is probably too weak to transform it into a more spherical or any higher-order symmetry.

Thus it is more likely that in the hydrated salt, the presence of ammonium ions may have caused the expansion of the lattice and in this manner reduced the extent of hydrogen bonding between the coordinated water molecules and the sulphate ions. Even though in terms of crystal energy this reduction is compensated for by the reformation of the hydrogen bonds between the ammonium ions and the sulphate ions, the reduction of the hydrogen bonding on the water molecules has the effect of reducing the electron density on the oxygen atoms. This would certainly result in the transformation of the water molecules into weaker ligands and hence a weaker ligand field. Thus $10Dq$ for hexaaquo complexes in the double salts should be smaller compared to those in the sulphate salts as reported here for Mn(II), Ni(II) and Zn(II).

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